

# Determination of total arsenic by photo-decomposition of organoarsenic compounds and hydride generation electrothermal atomic absorption spectrometry

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**Abstract**— A method was developed for the determination of total arsenic concentration in less than ng/ml level by decomposition of organoarsenicals using photo-oxidation combined with in situ trapping of arsenic hydride on a palladium coated graphite tube with subsequent atomization and detection by AAS. The organoarsenicals include monomethylarsenic, dimethylarsenic, arsenobetaine, arsenocholine, o-aminobenzenarsenate and p-aminobenzenarsenate. The method is simple and sensitive. Detection limit was obtained from different arsenic compounds over the range from 0.058 to 0.063 ng/ml as As (based on three times of the standard deviation of 10 blank measurements) and the relative standard deviations for ten replicate measurements were from 2.0 to 3.8%. The calibration curves of arsenic compounds including inorganic and organic arsenicals were linear over the range from 0.1 to 3.0 ng/ml as As. The recommended method has been applied to the determination of total arsenic in tap and lake water samples at ng/ml levels.

**Keywords:** electrothermal atomic absorption spectrometry; photo-decomposition; organoarsenic compounds; arsenic hydride generation; tap/lake water

## INTRODUCTION

Arsenic compounds are known to be naturally present in environment, these mainly include arsenite, arsenate, monomethylarsonate (MMA), dimethylarsonate (DMA), arsenobetaine (AsB), arsenocholine (AsC). Though in recent years a good deal of attention has been directed to the study of arsenic species (Ebdon, 1987; Ricci, 1981), however, most countries with arsenic regulatory standards set limitation only in total arsenic concentration currently. Hence, the total arsenic determination including organically bonded and inorganic arsenic is of foremost importance to most investigations, especially arsenic at sub-parts-per billion level. Derivatization by hydride formation and subsequent detection in the gaseous phase by atomic spec-

trometry has had immense impact on the determination of arsenic species at trace level. By adopting suitable generation conditions, it is possible to generate hydride quantitatively from arsenite, arsenate, MMA, DMA, but it is important to note that certain naturally occurring arsenic compounds, for instance, arsenobetaine, are not hydride-reactive species, i. e. they do not react with sodium borohydride to form volatile hydrides. Previous studies (Stinger, 1979; Cullen, 1988; Atallah, 1991) have shown that organoarsenicals can be decomposed by exposure to sufficient ultraviolet radiation from a high pressure mercury arc vapor lamp. This technique makes it possible for the conversion of organoarsenicals into hydride-reactive arsenics. The method has the advantages over conventional acid digestion methods, for example reduced analysis time, less contamination, simple operation and safe. D. A. Kalman (Atallah, 1991) reported the on-line oxidation of organoarsenicals to inorganic arsenic in a flow-injection analysis system. The arsenate generated by oxidation of organoarsenicals is reduced to arsine and detected by AAS. Calibration curves obtained for As(V), AsB and DMA solutions were over the concentration range 0.1–2.0 ppm.

In this paper, we present a sensitive method for the determination of total arsenic concentration in less than ng/ml level by decomposition of the organoarsenicals using photo-oxidation combined with in situ trapping of arsenic hydride on palladium coated graphite tube before atomization. Detection limits for different arsenic compounds were obtained over the range from 0.058 to 0.063 ng/ml of As (based on three times of the standard deviation of ten blank measurements) and the relative standard deviations for ten replicate measurements were from 2.0 to 3.8%. The calibration curves of different arsenic compounds were linear from 0.1 to 3.0 ng/ml as As.

## MATERIALS AND METHOD

### *Apparatus*

An FXW-1B atomic absorption spectrometer with a deuterium background corrector (China) equipped with an HGA-72 graphite furnace (Perkin-Elmer), pyrolytic graphite tube (Beijing Material Technology Institute) and a high intensity arsenic lamp (General Research Institute of Non-Ferrous Metals, Beijing, China) was used. A laboratory-made hydride generator was used, which is similar to those described previously (Zhang, 1989; Ni, 1991). Hydride generation was accomplished by using a two channel peristaltic pump to deliver the sample solution and sodium tetrahydroborate to the reaction vessel which served as a hydride generator. The hydride formed was stripped by argon from the solution and was introduced onto the

graphite tube via a quartz tube. The photoreactor unit is similar to those described by Stringer and Kalman (1979 and 1991). A high pressure 500 W mercury lamp is mounted vertically in the middle of aluminum cylinder which is large enough in diameter to accommodate sixteen 10 ml quartz tubes. A blower fan was attached to the bottom of the lamp to provide cooling for the lamp and samples. The unit is enclosed in aluminum foil for the maximum irradiation.

All the instrumental conditions are listed in Table 1.

**Table 1 Instrumental conditions**

Parameter	Value
Wave length	193.7 nm
Lamp current	5 mA
Spectral bandpass	0.4 nm
Recorder range	0.5 V
Carrier gas flow rate	0.1 ml/min
Acidity	3.0 mol/L HCl
Uptaken rate of sample solution	1.0 ml/min
Uptaken rate of 2% NaBH <sub>4</sub> solution	1.0 ml/min

### Reagents

Aqueous standard stock solutions (1 mg/ml as As) of As (III), As(V), MMA, DMA, o-aminobenzenarsenate, p-aminobenzenarsenate were prepared by dissolving arsenic trioxide (Johnson Matthey Chemical Limited, England); sodium arsenate (Beijing Chemical Industries, Beijing, China); Monomethylarsonic acid (MMA; Sigma Chemical Company); sodium dimethylarsonate (DMA; Sigma Chemical Company); o-aminobenzenarsonic acid (o-ABA; Sigma Chemical Company) and p-aminobenzenarsonic acid (p-ABA; Sigma Chemical Company) in deionized water, respectively. Arsenobetaine and arsenocholine were prepared from arsenobetaine hydrate and arsenocholine iodide provided by X. Le, Department of Chemistry, University of British Columbia and synthesized according to the method of J.S. Edmonds (Edmonds, 1977). They were standardized against As(III) by ICP-AES and flame AAS. The final standard solutions were obtained by diluting the above solutions in deionized water to 20 ng/ml in concentration. Sodium tetrahydroborate solution was prepared daily by dissolving NaBH<sub>4</sub> (Shanghai Chemical Reagent Factory, Shanghai, China) in deionized water and filtered before use. Potassium persulfate solution 2 mg/ml

(Guangzhou Chemical Reagent Factory, China. Purity is 99.9%) was freshly prepared before use.

All other reagents used were of analytical-reagent grade. Hydrochloric acid was prepared by subboiling distillation. The concentration of arsenic was checked before use.

### Procedure

#### Photo-oxidation

Place adequate amount of arsenic standard solution in a 10 ml quartz test tube, add 0.5 ml of 2 mg/ml potassium persulfate and dilute to 5 ml with deionized water. The test tubes closed with stoppers were positioned around the mercury lamp to be irradiated for 15 minutes in the photo-reactor system. After irradiation, the solution was diluted with 6 mol/L HCl to 10 ml and the final concentration of arsenic compound was generally 1 ng/ml as As.

#### Hydride generation GFAAS

The graphite furnace was operated using the program outlined in Table 2. The sequence of operations was as follows: 20  $\mu$ l 100 ppm Pd was added first into furnace as chemical modifier and after drying at 110 °C for 40 seconds, the tip of quartz tube from the outlet of hydride generator was inserted into the introduction port of graphite tube and held in contact with the opposite interior wall. The furnace temperature was increased to 700 °C and the peristaltic pump was then started to deliver the sample in 3 mol/L HCl and 2% NaBH<sub>4</sub> solution to the hydride generator at the same rate of 1 ml/min for 1 minute. The generated hydride was swept into the furnace through the quartz tube by argon at the rate of 0.1 L/min for 120 seconds. The quartz tube was then removed from the introduction port of the graphite tube and the signal was recorded as atomic absorbance at 2400 °C.

Table 2 Graphite furnace thermal programme

Programme	Temperature, °C	Ramp time, s	Hold time, s	Procedure
Drying	110	5	40	—
Adsorption	700	5	5	Insert quartz tube
			120	Hydride generation and collection
			5	Remove quartz tube
Atomization	2400	0	5	Atomization
Clean out	2500	0	5	—

## RESULTS AND ANALYSIS CONDITIONS

### *Optimization of analysis conditions*

Studies on the conditions required for optimization of signal in arsine-generation AAS, such as  $\text{NaBH}_4$  and HCl concentrations, have been well investigated (Zhang, 1989). Our experimental work confirmed those results in our experimental system, it was found that the sorption temperature and collection time for the hydride onto the graphite tube had no significant influence on the absorbance signals from 100 to 1000 °C and 70 to 180 seconds, respectively. The concentration of hydrochloric acid had also no influence from 1.0 to 6.0 mol/L while the concentration of  $\text{NaBH}_4$  was kept constant at 2% (w/v). The recommended conditions for hydride generation were 3 mol/L HCl, 2%  $\text{NaBH}_4$  solution, adsorption temperature 700 °C and collection time 120 seconds.

The temperature program for GFAAS is listed in Table 2.

### *Effects of photo-oxidation*

Application of the arsine generation technique is limited to arsenic species which can be reduced to arsine by  $\text{NaBH}_4$  in water solution. Some organoarsenicals do not react with  $\text{NaBH}_4$  to form volatile hydride. Therefore, in order to utilize the arsine generation technique for the determination of all arsenic species, the conversion of organoarsenicals into hydride-reactive arsenic is required. It has been reported that persulfate solution under ultraviolet irradiation undergoes photo-decomposition reaction giving highly reactive hydroxyl radicals which can result in the conversion of organic compound into carbon dioxide (Rosset, 1982). Some research groups have introduced this photo-decomposition technique for arsenic species analysis (Stinger, 1979; Cullen, 1988; Atallah, 1991). In our experiment the different responses of eight arsenic species were investigated by using the following detection methods: a. direct injection graphite furnace atomic absorption spectrometry; b. hydride generation graphite furnace atomic absorption spectrometry; c. photo-decomposition followed by hydride generation graphite furnace atomic absorption spectrometry. The observed results are listed in Table 3. The results indicated that all the arsenic species investigated exhibit almost the same response in the GFAAS analysis. Some of the species, such as As(III), As(V) and MMA are capable of direct detection by hydride generation system. But for the detection of DMA, AsB, AsC, o-ABA and p-ABA by hydride generation GFAAS, the photo-decomposition in the presence of persulfate is necessary. The results also confirmed that with ultraviolet irradiation all the species were completely converted into hydride reactive arsenic species.

Table 3 Response comparison of different arsenic species

Species	Absorbance		
	GFAAS <sup>*</sup>	Arsine generation /GFAAS <sup>**</sup>	Photo-oxidation HG/GFAAS <sup>*</sup>
As(V)	0.115	0.285	0.242
As(III)	0.115	0.295	0.252
MMA	0.115	0.295	0.250
DMA	0.112	0.145	0.240
o-ABA	0.105	0.020	0.253
p-ABA	0.090	0.010	0.230
AsB	0.080	0.010	0.230
AsC	0.080	0.010	0.245

\* 20  $\mu$ l of 20 ng/ml as As were injected. GFAAS: graphite furnace atomic absorption spectrometry.

\*\* 1 ml of 1 ng/ml as As was delivered to hydride generator. HG/GFAAS: hydride generation graphite furnace atomic absorption spectrometry.

#### Optimization of photo-oxidation conditions

Photo-oxidation conditions were optimized with 1 ng/ml as As in AsB, AsC, o-ABA and p-ABA. The effects of potassium persulfate concentration, reaction medium and irradiation time were evaluated independently. The results are shown in Fig. 1 to Fig. 3. Fig. 1 shows that without the presence of potassium persulfate, o-ABA and p-ABA are decomposed by photo-irradiation to over 80 per cent. The efficiency of photo-oxidation was complete for AsB and AsC when potassium persulfate concentration was above 0.2 mg/ml. Good recovery was obtained in neutral and basic solutions, but the recovery was not complete in acidic solutions as shown in Fig. 2. Irradiation time investigated for AsB is shown in Fig. 3. When the irradiation time is longer than 7 minutes the absorbance leveled out. The recommended conditions are 0.2 mg/ml potassium persulfate in neutral solution and 15 minutes for photo-irradiation time. Under these conditions, the detection limits were over the range from 0.058 to 0.063 ng/ml as As and the relative standard deviations for ten replicate measurements were from 2.0 to 3.8% (Table 4). The calibration curves of these arsenic compounds were linear from 0.1 to 3.0 ng/ml as As.

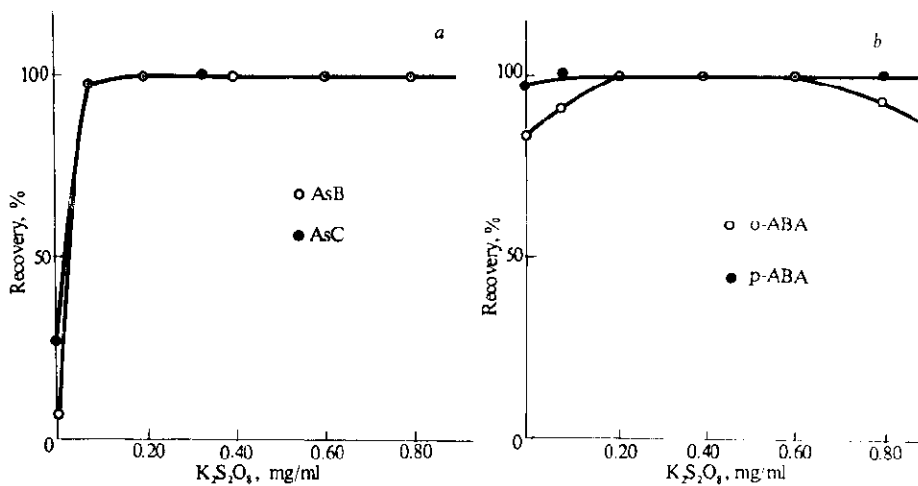


Fig. 1 Dependence of recoveries of organoarsenic compounds on the concentration of potassium persulfate. Photo-decomposition medium is neutral and irradiation time is 15 minutes

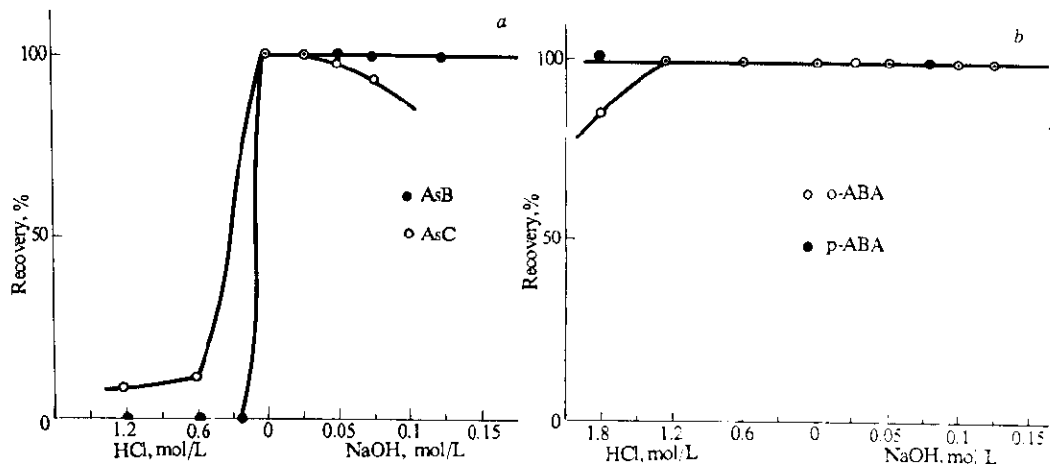


Fig.2 Effects of photo-decomposition medium on recoveries of organoarsenicals. Irradiation time is 15 minutes, potassium persulfate is 0.2 mg/ml

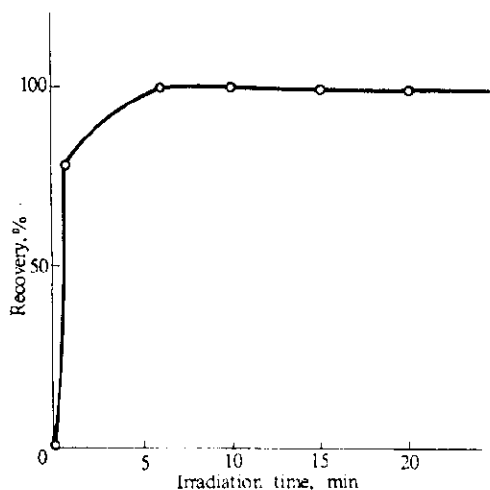


Fig.3 Dependence of the recovery of arsenobetaine on irradiation time photo-decomposition medium is neutral and potassium persulfate is 0.2 mg/ml

### Sample analysis

The method was applied to the analysis of tap and lake water (Kunming Lake, Beijing). The concentration of total arsenic in tap and lake water were 0.4 ng/ml and 1.1 ng/ml, respectively. Recovery results summarized in Table 5 indicate that recoveries of arsenic from different arsenic compounds are satisfactory.

Photo-decomposition combined with in situ trapping of hydride on a palladium coated graphite tube with subsequent atomization and detection by AAS is a sensitive and simple method for the determination of total arsenic. The method might be adopted to other hydride forming elements, such as lead and selenium.

Table 4 Detection limit and relative standard deviation

Species	Detection limit, ng/ml	Relative standard deviation, %
As(III)	0.058	3.8
As(V)	0.061	2.6
MMA	0.058	3.2
DMA	0.060	3.5
o-ABA	0.058	3.2
p-ABA	0.063	3.8
AsB	0.062	2.0
AsC	0.060	2.6



**Table 5 Recovery of arsenic from different arsenic compounds in tap and lake water**

Compounds	Recovery, %*	
	Tap water	Lake water
As(III)	101.2	97.5
As(V)	100.2	98.2
MMA	95.5	95.6
DMA	103.5	96.4
o-ABA	102.8	98.0
p-ABA	96.4	95.6
AsB	100.0	95.5
AsC	95.3	95.5
Mixed**	103.3	97.8

\* 1 ng/ml as As was added

\*\* 0.2 ng/ml as As in each arsenic compounds was added together

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